Isolation of Water-Miscible High-Oil Fractions from Starch-Oil Composites

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ABSTRACT

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High-oil fractions were isolated from a series of starch-oil composites prepared by jet-cooking mixtures of starch and vegetable oil in water. They consisted of an emulsion of starch, oil, and water. These fractions were miscible in water and nearly immiscible in hexane. Emulsions from composites prepared with 10–40% oil contained 40–75% of the oil found in the original composite. Oil content of the emulsions varied with the oil content of the original composite, but the ratio of water to starch was essentially constant.

A process for production of highly stable starch-oil composites (Fantesk) by steam jet-cooking mixtures of starches and lipids was recently reported by researchers at this laboratory (Eskins and Fanta 1994, Fanta and Eskins 1995). In this process, the combination of high temperature and pressure and the mixing action during passage of sample through a small orifice causes complete gelatinization and solubilization of the starch and intimate mixing of the starch with the lipid. These composites are water-dispersible over a wide range of dilution, from soft gels to dilute solutions, with no separation of phases, and they have substantial potential for use in low-fat food preparations. The composites can be dried to a free-flowing powder and reconstituted without significant alteration of their solubility characteristics.

Composites have been evaluated (Knutson et al 1996) to determine whether the cooking procedure results in alteration of the chemical composition of either the starch or the oil. No compositional changes in either starch or oil are apparent. Extraction of oil from dried composites with a variety of organic solvents is not effective for complete recovery of oil. An amount of oil representing ≈5% of the starting weight of the composite can only be recovered by hydrolytic degradation of the starch. Extraction of oil from aqueous solutions of composites is also inefficient for complete oil recovery. Typically, eight extractions with hexane recover ≈50% of the oil from a solution with starch concentration of 1.25%.

Eskins et al (1996) examined the ultrastructure of gels prepared from water suspensions of these composites by light microscopy and transmission electron microscopy and examined dried films by scanning electron microscopy. They found oil microencapsulated in the starch-water matrix as droplets of 1–10 μm diameter. The size and distribution of oil droplets are determined by oil-to-starch ratio of the composite and by mixing and cooking conditions. Transmission electron microscopy of gels shows that oil droplets are surrounded by a boundary layer different from the oil core, and also different from the surrounding starch matrix. This boundary layer has a relatively constant dimension regardless of droplet size. They suggested that this boundary layer might result from formation of amylose-lipid inclusion complexes at the starch-lipid interface, perhaps formed from trace amounts of monoglyceride either present in the oil or formed by deesterification of triglycerides under the high temperature and shear of the jet-cooking process.

During examination of high-oil composites (1:1 oil-to-starch ratios), we observed that dried samples, upon reconstitution in water, produced a low-density, oily liquid that rose to the surface of the solution. This fraction, which had not been observed in composites of lower oil-to-starch ratios (≤0.5:1), was not readily extracted with hexane. Analysis for carbohydrate (Knutson 1997) indicated a small amount of carbohydrate (presumably starch) was present. Addition of α-amylase destroyed the fraction and released a large amount of oil, verifying the presence of starch.

Finding this fraction in high-oil composites prompted further examination of composites with lower oil content, which remain homogeneous after redispersion in water, to ascertain whether, and to what extent, such fractions exist in more stable formulations. Experiments were conducted to collect high-oil fractions from various composites, to measure their oil and carbohydrate content, and to evaluate their importance in the solution stability of the composites.

Composites containing 10, 20, 30, and 40% added oil were prepared by passing vigorously stirred mixtures containing 30, 60, 90, and 120 g of vegetable oil and 300 g (db) of unmodified food-grade common corn starch in 1 L of water through a Penick and Ford jet-cooker with steam at a line pressure of 65 psi and outlet pressure at 40 psi. The product was collected in Dewar flasks to maintain temperature and prevent retrogradation, then dried on a drum dryer heated with steam at 30 psi.

Oil content of composite samples was determined as reported by Knutson et al (1996). Sample was redispersed in water, heated to boiling, and cooled to room temperature. α-Amylase was added to hydrolyze starch and release the oil. After completion of hydrolysis, solution was extracted three times with 0.5 volumes of hexane. Hexane was evaporated, and oil was determined gravimetrically.

High-oil low-density fractions were collected from composites by centrifugation. For compositional analysis, samples (4 g) of dried composites (in duplicate) were mixed with 80 mL of water, heated to boiling, cooled to room temperature, and centrifuged at 2,800 × g. Composites containing 20 and 40% added oil were centrifuged for periods of 15, 30, 45, and 60 min. Composites containing 10 and 30% added oil were centrifuged 60 min. In all samples, a tan opaque emulsion collected at the surface along with a small amount of free oil. Free oil was removed by flooding the surface with hexane, gently stirring, and aspirating the hexane layer from the surface. Emulsion was skimmed from the top of the tubes, transferred into a 12-mL centrifuge tube and washed with 2 mL of water. Emulsion mixed readily with water, but because of its low density, it gradually separated upon standing. Mixture was centrifuged 1 min at 2,800 × g and the aqueous layer was removed from the bottom of the tube by pipette. Emulsion was washed four times, at which point the aqueous layer was clear and its carbohydrate content was negligible. Weight of emulsion was recorded, and 10 μL (80 units) of α-amylase was added to the sample. Emulsion began to dissipate immediately, with oil appearing at the surface. Hydrolysis was allowed to continue overnight. Sample was centrifuged, and the clear oily upper layer was removed by multiple ex-

tractions with hexane. Hexane was evaporated and oil was determined gravimetrically. Three extractions were sufficient to obtain constant weight of oil. The residual aqueous layer was weighed and assayed for carbohydrate using the phenol-sulfuric acid assay (Dubois et al 1956).

Residual solution of the original composite was hydrolyzed with α-amylase to liberate retained oil not removed by centrifugation. After completion of hydrolysis, solution was extracted with hexane to recover residual oil, which was determined gravimetrically.

Table I shows the total oil content for 20 and 40% added oil samples; the amount of oil removed by centrifugation for 15, 30, and 60 min, both as free oil and as water-miscible emulsion; and the amount retained in the aqueous solution. With longer centrifugation time, the amount free oil increased, and the amount of oil retained in the aqueous layer decreased until a constant state was reached between 45 and 60 min. For samples centrifuged >15 min, the major portion of oil was located in the emulsion.

Table II shows oil, water, and starch content of each emulsion. Oil content, both as total weight and as a proportion of the weight of the emulsion, increased with increasing oil content of starting composite. Water and carbohydrate content diminished proportionately. Ratio of water to carbohydrate was 12.3 for emulsion from the 10% composite and 19.3, 18.3, and 22.9 for 20, 30, and 40% composites, respectively. Mean value was 20.2.

Preparative-scale samples of emulsion from 20 and 40% composites were isolated by the same procedure starting with 32 g of composite (Fig. 1). These were used to quantitatively evaluate the hexane extractability of oil from emulsions. A portion of emulsion was immersed in 5 mL of hexane and stirred thoroughly. Emulsion resisted mixing with hexane, so hexane was easily aspirated from top of the mixture. Hexane was evaporated to dryness and extracted oil determined quantitatively. The process was repeated 12 times for each sample. Although emulsions were permeable to hexane, the extraction was inefficient. The amount of oil extracted for each successive extraction was essentially constant. From 4.2 g of emulsion from a 20% composite containing 2.5 g of oil, a mean of 64 mg was obtained per extraction, with a standard deviation of 16 mg, a total of 770 mg for 12 extractions, which was 30% of the initial weight of oil. From 9.5 g of emulsion from a 40% composite containing 6.2 g of oil, 93 mg of oil was obtained per extraction, with a standard deviation of 21 mg, a total of 1,120 mg for 12

extractions, which was 18% of the initial weight. Determination of carbohydrate and water content of a sample of the 40% emulsion before and after 12 extractions, showed an increase proportional to the loss of oil, with the ratio of water to carbohydrate unchanged.

To evaluate stability of the pure emulsion in the absence of the protective barrier provided by the starch matrix present in composite solutions, 500 mg of emulsion from 20% composite was spread as a thin film on a petri dish and left exposed to the air at room temperature. After overnight exposure, water was totally evaporated and the emulsion disrupted. Oil was readily and quantitatively extractable with hexane, leaving 12.2 mg of residue, which was identified and quantitatively determined as starch by measurement of total carbohydrate (Dubois et al 1956) and amylose content (Knutson 1986). Carbohydrate content of the residue was 96.2%; amylose content was 21.7%.

The constant ratio of starch to water in these emulsions, the variation of their oil content with that of the original composite, and the stabilization of the emulsion by the presence of starch in the aqueous phase all suggested that the emulsions consisted of discrete droplets of oil surrounded by a starch-water boundary, equivalent to the condition described by Eskins et al (1996) for gels of starch-oil composites. To evaluate the feasibility of such a composition, the expected oil-to-water ratios were calculated for spherical oil droplets of 1–10 μm diameter, all with boundary layers with a constant thickness of 0.6 μm, assuming oil density of 0.92 and starch density of 1.55. Estimated densities of boundary layers, based on the ratio of starch to water found in each of the four emulsion compositions studied, were 1.12 for emulsion from the 10% composite, 1.08 for the 20 and 30% composite, and 1.07 for the 40% composite. Using an average density of 1.09, ratios of oil to water were calculated to be 0.09 for a 1-μm droplet, 0.48 for for a 3-μm droplet, 1.16 for a 6-μm droplet, and 2.09 for a 10-μm droplet. These values were compatible with the oil-to-water ratios for emulsions from composites included in this study (Table II). Based on those oil-to-water ratios, average diameters of oil droplets were estimated to be 2.1, 3.9, 4.6, and 8.7 μm, for emulsions from 10, 20, 30, and 40% composites, respectively, which is consistent with the transmission electron micrographs of composite gels shown by Eskins et al (1996).

TABLE I
Centrifugation Time and Distribution of Oil in Composite Fractions

	20% Added Oil[a]			40% Added Oil[a]		
	15 min	30 min	60 min	15 min	30 min	60 min
Total oil (mg/g of composite)	137.7	137.7	137.7	259.6	259.6	259.6
Free oil	7.6	10.0	16.9	19.7	32.1	33.7
Emulsion oil	42.5	80.6	97.7	176.8	179.0	188.6
Retained oil	87.0	46.5	21.8	63.2	48.5	37.3

[a] Amount of oil in each formulation (% of weight of starch in a 30% starch paste).

TABLE II
Composition of Emulsion Isolated from Composites of Varying Oil Content

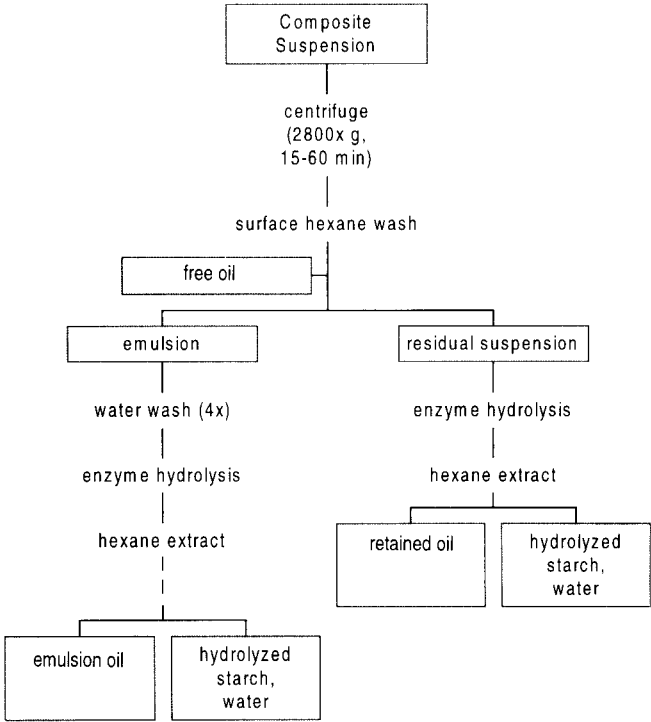|	Composite (% added oil)			
	10	20	30	40
Oil content (mg/g of composite)	67.9	136.4	203.9	259.6
Oil in emulsion (mg)	27.6	97.7	152.8	188.6
Total oil in emulsion (%)	40.6	71.6	74.9	72.7
Proportion of components				
Oil	22.5	41.2	45.9	64.0
Water	71.8	55.9	51.3	34.4
Starch	5.8	2.9	2.8	1.5
Oil-to-water ratio	0.3	0.7	0.9	1.9

Fig. 1. Flow diagram of emulsion recovery procedure.

The presence of a significant portion of retained oil in the major aqueous fraction after centrifugation can be satisfactorily explained as being due to emulsified particles containing extremely small oil droplets. As size of the oil droplet decreases, a boundary area of a constant diameter becomes proportionally larger, resulting in a correspondingly higher density. As the density of the particle approaches that of water, separation by centrifugation under the conditions used in this study is precluded. Indeed, given the amount of starch with density of 1.5 present in the aqueous layer, emulsion particles with a density greater than that of water are theoretically possible.

These results provide a preliminary characterization of a water-miscible fraction obtained from jet-cooked starch-oil composites and a possible explanation for the stability of such composites that is consistent with the hypotheses suggested by Eskins et al (1996). Oil-to-water ratios were consistent with droplet size reported by those workers, and the oil content of emulsions varied with oil content of original composite, consistent their observation that average droplet size varied directly with oil content of the composite. The hydrophilic nature of the boundary layer surrounding the oil droplets would enable them to mix freely in aqueous media and to remain suspended indefinitely in the starch-water matrix, with the viscosity of the surrounding matrix serving to inhibit gravitational separation and thus maintaining the suspension.

Investigation of these emulsions is continuing; we are seeking to: 1) ascertain whether emulsions will separate spontaneously with sufficient dilution and corresponding viscosity reduction; 2) examine emulsions from composites prepared under conditions that affect droplet size to see whether larger amounts of emulsion with relatively low oil content can be obtained; 3) investigate higher oil composites to determine the upper limit of oil content compatible with solution stability; and 4) attempt to observe discrete particles in emulsions by microscopic methods.

LITERATURE CITED

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F. 1956. Colorimetric method for determination of sugars and related substances. Anal. Chem. 28:350-356.
Eskins, K., and Fanta, G. F. 1994. Starch-oil compositions by steam jet cooking. U.S. patent application.
Eskins, K., Fanta, G. F., Felker, F. C., and Baker, F. L. 1996. Ultrastructural studies on microencapsulated oil droplets in aqueous gel and dried film of a new starch-oil composite. Carbohydr. Polym. 29:233-239.
Fanta, G. F., and Eskins, K. 1995. Stable starch-lipid compositions prepared by steam jet cooking. Carbohydr. Polym. 28:171-175.
Knutson, C. A. 1986. A simplified colorimetric procedure for determination of amylose in maize starches. Cereal Chem. 63:89-92.
Knutson, C. A., Eskins, K., and Fanta, G. F. 1996. Composition and oil-retaining capacity of jet-cooked starch-oil composites. Cereal Chem. 73:185-188.
Knutson, C. A. 1997. Use of phenol-sulfuric acid assay to determine composition of starch-oil composites. Cereal Chem. 74:471-472.